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# Hydrodechlorination of dichloromethane with mono- and bimetallic Pd–Pt on sulfated and tungstated zirconia catalysts

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# ABSTRACT

Monometallic (Pt or Pd) and bimetallic (Pt–Pd) catalysts supported on zirconia promoted with sulfate (SZ) or tungsten oxide (WZ) were prepared and tested in the gas-phase hydrodechlorination of dichloromethane. The catalysts showed a high selectivity to non-chlorinated products (between 80% and 90% at 250 °C) being methane the main reaction product. As a general trend, the WZ catalysts yielded significantly higher dichloromethane conversion than the SZ ones, yielding all the catalysts initial conversions higher than 80% at a reaction temperature of 250 °C. However, the former showed a very poor stability regardless of the metallic active phase. On the other hand, the presence of palladium in the sulfated zirconia catalyst avoids deactivation as proved in long-term experiments (80-h time on stream). XPS and elemental analyses of the used catalysts suggest that adsorption of organochlorinated species is a cause of deactivation by blocking the active sites. In the monometallic SZ Pt catalyst, deactivation occurs also by poisoning of the Pt sites by the H<sub>2</sub>S resulting from sulfate reduction under the hydrogen-rich gas atmosphere. The metal particle size appears to be a critical point with regard to stability of the catalysts. The one with the highest dispersion showed the highest stability with no signs of deactivation after more than 80 h on stream.

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# 1. Introduction

The emission of chlorinated volatile organic compounds (CVOCs) to the atmosphere contributes to ozone depletion, photochemical smog formation, and global warming [1–3]. In particular, dichloromethane (DCM) is used as solvent in the chemical and pharmaceutical industries in the synthesis of different chemical compounds and polymers and for paint stripping and degreasing operations. Among the different removal techniques, catalytic hydrodechlorination (HDC) shows potential economic and environmental advantages when compared with other techniques.

In the last years, much effort has been focused in the study of the catalytic hydrodechlorination of CVOCs by catalysts based on different metals and supports. However, in the studies analyzing the gas-phase deep hydrodechlorination of chloroform and dichloromethane with supported metallic catalysts, either a rapid deactivation has been reported or simply long-term experiments were not performed [4–13]. The stability of the hydrodechlorination catalysts is a key feature for industrial applications. Deactivation has been attributed to poisoning by HCl and chlorinated organic species, coke formation (in some cases including chlorine in its composition), loss of metal through the formation of volatile compounds and metal sintering, changes in the metallic oxidation state and metal migration [10,14–20]. The support plays a significant role in the activity and the stability of the catalysts [4–21], its surface acidity seems to play a key role in deactivation.

Our research group has previously investigated the gas-phase hydrodechlorination of dichloromethane and chloroform using Pd on activated carbon (Pd/C) catalysts, which showed high activity and high selectivity to non-chlorinated products [22-26]. However, these catalysts underwent significant deactivation due to the irreversible chemisorption of reactants and/or reaction products on the active sites. A comparative study [23] on the behavior of Pd, Ru, Pt, and Rh catalysts supported on activated carbon in the hydrodechlorination of DCM showed that Pd/C and Rh/C were the most active catalysts but Pt/C showed the highest stability with no sign of deactivation after 65 h on stream. More recently [27], a Pt/C catalyst prepared in our lab showed a very high stability with no significant loss of activity after 26 days on stream, which had not been previously reported. It seems that a high  $Pt^{0}/Pt^{n+}$  ratio favors the stability of the catalyst since Pt<sup>0</sup> appears to be more resistant than  $Pt^{n+}$  to poisoning by organochlorinated compounds. The  $Pt^0/$  $Pt^{n+}$  ratio can be controlled with the reduction temperature. Higher reduction temperatures lead to a higher proportion of zerovalent platinum, although at reduction temperatures higher than around 250 °C, an agglomeration of the metal particles can take place with



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the consequent decrease in dispersion. Based on preliminary studies [28], we have selected a proper reduction temperature in order to obtain catalysts with a high Pt<sup>0</sup>/Pt<sup>n+</sup> ratio and with low metal particle sizes. On the other hand, re-dispersion of metal particles was observed in the Pt/C catalyst [27] leading to non-agglomerated small particles well distributed on the support, which contribute to increase the concentration of H<sub>2</sub> in the vicinity of the active sites and its spillover in the catalytic surface. This appears to favor the reaction of H<sub>2</sub> with the adsorbed chlorinated hydrocarbons, thus inhibiting the poisoning of the catalyst [27]. Therefore, the high resistance of Pt/C to poisoning by these compounds when compared to other catalysts reported in the literature can be attributed to redispersion of Pt during the reaction leading to much smaller metal particles with a very homogeneous size distribution, showing very little agglomeration and being well distributed over the support. It is proposed that these factors would inhibit the formation and stabilization of hydrocarbons other than CH<sub>4</sub> at the active centers.

In order to confirm the role of the metallic particle size and distribution over de support in the stability of the catalysts in the HDC of chloromethanes, in this work, the performance of catalysts prepared from supports with a very different nature than that of carbon, but allowing a wide range of dispersions of the active phase, is investigated. This may contribute to improve rational design of future catalysts.

Taking into account the key role of the acidity of the support in the dispersion of the metallic phase and the deactivation of the catalysts, it is of interest to investigate the development of catalysts with a good balance between the metallic and acidic functions. The objective of this work is to analyze the activity, selectivity, and stability of different mono- and bimetallic Pd–Pt catalysts based on acidic supports, like sulfated (SZ) and tungstated (WZ) zirconia, in the hydrodechlorination of dichloromethane. The selection of metals was made by considering the great stability of Pt and the high activity of Pd [23,27]. Moreover, the use of bimetallic catalysts often results in an increase in the metallic dispersion. In fact, the novel catalytic system SZ Pt–Pd reported in this study shows the same stability and selectivity that our previous Pt/C catalysts [27] but with a significant increase in activity.

# 2. Experimental

## 2.1. Catalyst preparation

Monometallic (Pd or Pt) and bimetallic (Pd and Pt) catalysts were supported on sulfated and tungstated-promoted zirconia. The  $SO_4^{2-}$ -ZrO<sub>2</sub> support (SZ) was obtained from commercial material in the form of a powdered sulfate-doped hydroxide gel (SZOH) (Grade XZO 1249/01, 7.6 wt.% S on ZrO<sub>2</sub> basis) and the WO<sub>3</sub>-ZrO<sub>2</sub> support (WZ) was obtained from commercial material in the form of a powdered tungstated-doped hydroxide gel (WZOH) (Grade XZO 1251/01, 16 wt.% W on ZrO<sub>2</sub> basis). Both commercial materials were supplied by MEL Chemicals. These supports were first pressed and shaped into cylindrical pellets using a hydraulic press (8 Ton cm<sup>-2</sup>). Then, the pellets were ground and sieved to 35–80 meshes. Samples were taken and subjected to calcination in a muffle furnace in static air for 3 h at 600 °C in the case of SZOH and at 800 °C in the case of WZOH, temperatures that were confirmed in previous studies as optimal for obtaining a crystalline tetragonal zirconia with a proper amount of acidic sites [29,30]. In each calcination treatment, the catalyst was first heated from room temperature to 180 °C at 2 °C min<sup>-1</sup> in air and this temperature was held for 1 h. Then, the temperature was increased at a heating rate of 5 °C min<sup>-1</sup> up to 600 °C or 800 °C and held for another 3 h. The sample was then cooled down to room temperature.

The resulting crystalline solids (SZ and WZ, for sulfated and tungstated zirconia supports, respectively) were then impregnated at room temperature with chloroplatinic acid (H<sub>2</sub>Cl<sub>6</sub>Pt·6H<sub>2</sub>O, Sigma-Aldrich, <99.9%, CAS Number: 26023-84-7) and/or palladium chloride (Cl<sub>2</sub>Pd, Sigma–Aldrich, <99.9%, CAS Number: 7647-10-1) aqueous solutions by the incipient wetness method. The amount of solution was regulated to obtain nominal 0.5% Pt or Pd in the final catalyst. Once impregnated, the samples were maintained 24 h at room temperature and then dried slowly in a stove. The temperature was raised slowly from ambient to 110 °C in order to prevent the solvent carrying over the metal precursor to the pore mouths. The samples obtained were denoted as SZ Pd and SZ Pt for the palladium and platinum sulfated zirconia, respectively, and WZ Pd and WZ Pt for the palladium and platinum tungstated zirconia, respectively. In the case of the bimetallic catalysts, the supports (SZ and WZ) were impregnated first with a chloroplatinic acid solution by the incipient wetness method.

Then, the impregnated samples were maintained 24 h at room temperature, subsequently dried at 120 °C and finally calcined in air for 1 h at 500 °C to assure the removal of water and the decomposition of the metallic precursor. Afterward, incipient wetness impregnation was accomplished with palladium chloride solution. Once again, the impregnated samples were maintained 24 h at room temperature, subsequently dried at 120 °C and finally calcined in air for 1 h at 500 °C to assure the removal of water and the decomposition of palladium chloride. The concentrations of Pt and Pd in the impregnation solution were adjusted in order to get a nominal 0.325% Pt and 0.175% Pd in the final catalyst. These weight percentages yield a Pt/Pd atomic ratio of 1:1. The samples obtained were named SZ Pd–Pt and WZ Pd–Pt, for the bimetallic catalysts supported on sulfated and tungstated zirconia, respectively.

# 2.2. Catalyst characterization

The pore structure of the catalysts fresh and once used in the HDC reaction was characterized from 77 K N<sub>2</sub> adsorption–desorption using a Micromeritics TriStar apparatus. The samples were previously outgassed for at least 8 h at 150 °C at a residual pressure of  $10^{-3}$  Torr. From the N<sub>2</sub> adsorption–desorption isotherms, the apparent surface area ( $A_{\text{BET}}$ ) was determined applying the BET equation [31] and the total pore volume was calculated from the amount of nitrogen adsorbed (as liquid) up to a relative pressure of 0.95.

The X-ray diffraction (XRD) patterns of the catalysts and supports were obtained in a X'Pert PRO Panalytical Diffractometer. The powdered sample was scanned using Cu K $\alpha$  monochromatic radiation ( $\lambda$  = 0.15406 nm) and a Ge mono filter. A scanning range of  $2\theta$  = 20–75° and scan step size of 0.020° with 5 s collection time were used.

The elemental analyses of the samples were performed in a Leco CHNS-932 system. The chemical analysis of Pt and Pd content of the solids was determined by atomic emission spectroscopy (ICP-AES) using an ARL model 3410 equipment. The solids were dissolved in a digestive pump with a mixture of 1 mL sulphuric acid, 3 mL hydrochloric acid, and 1 mL nitric acid. The surface of the catalysts was analyzed by X-ray photoelectron spectroscopy (XPS) with a Physical Electronics 5700C Multitechnique System, using Mg K $\alpha$  radiation (*hv* = 1253.6 eV). To determine all the elements present on the catalyst surface, general spectra were recorded for the samples by scanning the binding energy (BE) from 0 to 1200 eV. Binding energy values were corrected for the effects of sample charging by taking the C 1s peak (284.6 eV) as an internal standard. The accuracy of the BE scale was ±0.1 eV. The deconvolution procedure involved smoothing, a Shirley background subtraction, and curve fitting using mixed Gaussian-Lorentzian functions by a leastsquares method. The atomic ratios of the elements were calculated from the relative peak areas of the respective core level lines using Wagner sensitivity factors [32].

Micromeritics ChemiSorb 2705 pulse analyzer was used to measure the catalysts dispersion by CO chemisorption at room temperature. Several pulses of 50  $\mu$ L CO were then introduced until saturation of the catalyst surface was achieved. The number of exposed metallic atoms was calculated from CO chemisorption data. The stoichiometry of the adsorption of CO over the metallic atoms was assumed to be 1 [33,34].

XRD, XPS, CO chemisorption, and 77 K  $N_2$  adsorption–desorption were performed with the catalysts calcined at 450 °C under air flow, subsequently reduced at 300 °C for 2 h under hydrogen flow and then cooled down to room temperature under helium flow.

The reducibility of the metallic phase of the catalysts was analyzed by temperature-programmed reduction (TPR) in an Ohkura TP2002 apparatus equipped with a thermal conductivity detector. The samples (0.15 g) were first activated by calcination in air at 450 °C. Then, they were stabilized in Ar at 100 °C, cooled to room temperature, and finally heated to 800 °C at a 10 °C min<sup>-1</sup> rate in a stream of 4.8% H<sub>2</sub> in Ar.

# 2.3. Catalytic activity experiments

The activity of the catalysts in the hydrodechlorination of dichloromethane was evaluated in a continuous flow reaction system described elsewhere [22], consisting basically of a 4.0 mm i.d. guartz fixed-bed micro-reactor (Microactivity Reference, PID Eng&Tech, Spain) coupled to a gas chromatograph (Varian, model 450GC) equipped with a FID detector and a capillary column (Varian, CP-SilicaPLOT, 60 m) for the analysis of the reaction products. The catalysts were treated "in situ" by calcination in air at 450 °C (50 N cm<sup>3</sup> min<sup>-1</sup>) and reduction in hydrogen stream (50 N cm<sup>3</sup> min<sup>-1</sup>) for 1 h at 300 °C prior to reaction. The experiments were performed at atmospheric pressure using an inlet total flow rate of 100 N cm<sup>3</sup> min<sup>-1</sup> and a  $H_2/DCM$  molar ratio of 100 at a space time of 0.8  $kg_{cat}$  h (mol DCM)<sup>-1</sup>. The gas feed contained a DCM concentration of 1000 ppmv and was prepared by mixing appropriate proportions of a commercial mixture of dichloromethane and N<sub>2</sub> (4000 ppmv of DCM in  $N_2$ ) with pure  $N_2$ . Reaction temperatures within the range of 150-250 °C were tested. For the sake of checking possible mass-transfer limitations, a previous series of experiments was performed at 250 °C varying the total flow rate and the catalyst particle size. No significant changes were found in DCM conversion for gas velocity and particle size within the ranges of 0.02-0.06 m/s and 0.25-0.71 mm, respectively. The behavior of the catalysts was analyzed in terms of DCM conversion (X) and selectivities to the different reaction products  $(S_i)$ . The evolution of the catalytic activity upon time on stream was also studied. The carbon mass balances were checked and they matched always within 91-99%. The experimental results were reproducible with less than 5% error.

# 3. Results and discussion

#### 3.1. Catalyst characterization

Table 1 reports the BET surface area and total pore volume of the catalysts prepared. The  $N_2$  adsorption–desorption isotherms correspond to type IV of IUPAC classification characteristic of mesoporous solids with low contribution of microporosity as indicated by the low amount of nitrogen adsorbed at low relative pressures. The catalysts based on SZ support show a more developed porosity than the WZ-based as indicate the higher values of surface area

Table	1	
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Porous structure	of the catalysts.
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Catalyst	$A_{\rm BET}$ (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)
SZ Pt	116	0.176
SZ Pd	113	0.173
SZ Pt-Pd	112	0.175
WZ Pt	47	0.119
WZ Pd	48	0.122
WZ Pt-Pd	49	0.121

and pore volume, probably a consequence of the lower activation temperature (600 °C) of the SZOH hydroxide gel compared to that of the WZOH hydroxide gel (800 °C). No significant differences can be observed between the catalysts prepared with the same support.

Fig. 1 shows the TPR profiles of the supports and catalysts. The SZ series shows only the peaks associated with the reduction of the metallic species. That of SZ Pt displays a peak associated with the reduction of the platinum species at 166 °C and the TPR profile of SZ Pd shows a peak centered at 102 °C with a shoulder 116 °C, related to the reduction of palladium. This indicates a stronger interaction of platinum with the support. In the case of the bimetallic SZ Pt-Pd catalyst, it appears only one peak, centered at around 116 °C. Besides, the absence of peak at 166 °C in the TRP profile of SZ Pt-Pd catalyst indicates that there exists some kind of interaction between both metals. This type of interaction between Pd and Pt has been previously reported in bimetallic silica-alumina-supported catalysts [35,36]. It is possible that the metal precursor reduced firstly. which according to the TPR profiles of the monometallic samples should be palladium, can supply dissociated hydrogen that contributes to the reduction of the second metal (platinum). The TPR profiles of WZ catalysts show several peaks of metal reduction that



Fig. 1. TPR profiles of the supports and catalysts.

#### Table 2

Surface concentration (by XPS) of Pt and Pd (wt.%) and metal dispersion (%) of the catalysts prepared.

Catalyst	%Pd	%Pt	D (%)
SZ Pt	-	0.6	19
SZ Pt-Pd	1.0	0.7	28
SZ Pd	0.8	-	16
WZ Pt	-	0.6	14
WZ Pt-Pd	0.6	0.3	12
WZ Pd	0.7	-	16

denotes a higher heterogeneity in the location of metal particles onto the support. In contrast to the SZ series, the catalysts containing Pd show a reduction peak at higher temperature than that of Pt (maxima at 168 °C and 145 °C, respectively). On the other hand, these WZ catalysts, specially the WZ Pd, show a negative peak at temperatures between 111 °C and 129 °C, which can be attributed to hydrogen desorption from decomposition of mobile palladium hydrides previously formed [37,38], indicative of the reduction of metallic particles at low temperature. In the case of the SZ Pd catalysts, there is no evidence for Pd hydride decomposition probably as a consequence of the different type of interaction of Pd and the two different supports SZ and WZ. The peaks displayed above 300 °C correspond to the reduction of tungsten oxide species [39].

The chemical analysis (ICP) confirmed that the percentage of Pt and Pd was not modified by calcination and/or reduction treatments and that the real content lied within ±5% of the theoretical value calculated from the amount of impregnating precursor. Table 2 summarizes the elemental mass surface concentrations of Pt and Pd obtained by XPS. As can be seen, the mass surface concentration of platinum in the monometallic catalysts (0.6%) is only somewhat higher than the bulk one (0.5%) while important differences are observed for the bimetallic and SZ Pd catalysts, more noticeable for the SZ Pt-Pd that yielded mass surface concentrations of palladium and platinum significantly higher than the corresponding bulk contents. This indicates that the metal particles must be predominately located in the most external surface of the catalyst (since XPS allows to determine only the chemical composition of the outermost layer) approaching to an egg-shell type distribution. It is also worth mentioning that despite the use of chlorine-containing precursors (chloroplatinic acid and palladium chloride), no surface chlorine was detected in the XPS analyses of the SZ samples in contrast to the around 0.5 wt.% detected for the WZ catalysts.

The Pt 4f region of the XPS spectra for all the catalysts showed a doublet corresponding to Pt  $4f_{5/2}$  and Pt  $4f_{7/2}$  [40]. The separation between Pt  $4f_{5/2}$  and Pt  $4f_{7/2}$  peaks, due to spin orbital splitting, is a quantized value of 3.33 eV. The Pt  $4f_{7/2}$  peak lying at around 71.0 eV can be attributed to Pt<sup>0</sup> (zerovalent Pt), while the Pt  $4f_{7/2}$  peak located at around 72.3 is related to Pt<sup>n+</sup> (electrodeficient Pt).



Fig. 2. Deconvoluted Pt 4f spectra of the SZ Pt-Pd catalyst.

Table 3						
Pt <sup>0</sup> /Pt <sup>n+</sup>	atomic	ratio o	n the	surface	of the	catalysts.

	Pt <sup>0</sup> /Pt <sup>n+</sup>
SZ Pt	3.0
SZ Pt–Pd	4.8
WZ Pt	7.9
WZ Pt-Pd	4.3

Fig. 2 represents the deconvoluted Pt 4f spectra of the SZ Pt-Pd catalyst. Pt in this catalyst is present mainly as Pt<sup>0</sup>, with a lower fraction of  $Pt^{n+}$ . The values of the atomic ratio of surface platinum species (Pt<sup>0</sup> and Pt<sup>n+</sup>) for the different platinum-containing catalysts, as obtained by deconvolution of the XPS Pt 4f region, are summarized in Table 3. As can be seen, Pt<sup>0</sup> is by far the predominant state in all the cases as a result of the reduction step. It would be also interesting to deconvolute the Pd 3d spectra. However, in the case of the catalysts containing Zr and Pd, the Pd 3d<sub>5/2</sub> and Zr 3p<sub>3/2</sub> XPS spectra are overlapped. Some authors [41,42], which used Pd (1 wt.%) supported on zirconia catalysts, subtract the contribution of the Zr 3p signal from the total spectra and associate the rest of the spectra to the Pd 3d response, which could be deconvoluted. However, in this study, with fairly low palladium contents (0.5 wt.% for monometallic and 0.175 wt.% for bimetallic catalysts), this method does not allow obtaining reliable results of the relative amounts of zerovalent and electrodeficient palladium.

The XRD patterns of the catalysts are represented in Fig. 3. All the diffractograms showed the main peaks of monoclinic (m- $ZrO_2$ ) and tetragonal (t- $ZrO_2$ ) phases of zirconia [43]. In the case of the WZ catalysts, the main peaks associated with WO<sub>3</sub> phase are observed. The peaks associated with oxides of platinum and palladium was not seen in any of the diffractograms, whether due to the absence of metal oxide particles in these samples or



Fig. 3. XRD patterns of the catalysts.

because those particles are too small or non-crystalline. According to the XPS results, a small amount of metal oxide particles could be expected (Table 3). The peaks associated with zerovalent platinum and zerovalent palladium are located at  $2\theta$  values of  $39.8^{\circ}$  and 40.1°, respectively [44]. Fig. 4 shows more in detail the XRD spectra of the catalysts within the  $2\theta$  range of  $39-41^{\circ}$ . The peaks corresponding to zerovalent platinum or zerovalent palladium were not observed in the spectra of SZ catalysts. This suggests that the metal particles are of small size and relatively well dispersed, so they do not produce XRD reflections. However, Fig. 4 shows clearly peaks at  $2\theta$  = 39.8° related to Pt<sup>0</sup> in the WZ Pt and WZ Pt-Pd catalysts. This indicates that these catalysts contain larger platinum particles and suggests a poorer metal dispersion. The lower acidity of WZ compared to SZ [45] support may explain that poorer dispersion since it is well known that acidic groups increase the hydrophilic character of the support, thus favoring the diffusion of the metal precursor [46-48].

These results are in agreement with the metal dispersions obtained by CO chemisorptions reported in Table 2 where the lowest dispersion values are associated with the WZ Pt and WZ Pt–Pd catalysts, the ones with the highest metal particle sizes as suggested by the XRD diffractograms. Furthermore, the catalyst with the highest metal dispersion and consequently the lower metal particle size is the SZ Pt–Pd. Although CO chemisorption cannot distinguish between Pd and Pt and possible bimetallic formation can complicate matters further in terms of CO uptake, the significant higher dispersion value indicates lower particle sizes whether in monometallic or in bimetallic form.

# 3.2. Catalytic activity

The absence of mass-transfer limitations at the reaction conditions was verified. The external diffusion mass-transfer resistance was evaluated by the estimation of the Damköhler number [49]. The influence of internal mass transfer was evaluated using the Wheeler–Weisz dimensionless number [50], according to which internal mass-transfer effects can be neglected for values of the dimensionless Wheeler–Weisz number lower than 0.15 [50]. In the most unfavorable conditions, the values of the Damköhler and Wheeler–Weisz numbers fall well below 0.1 and 0.15, respectively, within the temperature range used in this work, thus allowing to neglect mass-transfer limitations in our experimental conditions according to the Carberry criterion [49]. Taking into account the low DCM concentration, it can be assumed that thermal effects are negligible.

Fig. 5 shows the values of DCM conversion obtained at a space time of 0.8 kg<sub>cat</sub> h (mol DCM)<sup>-1</sup> and different reaction temperatures with the SZ and WZ catalysts. A dramatic increase in conversion with temperature was observed within the range explored (150–250 °C). As can be seen, with the exception of the monometallic Pt catalysts, the WZ series yielded significantly higher DCM conversion than the SZ, although the differences become lower as the temperature increases. The bimetallic WZ Pt–Pd catalyst allowed almost complete DCM conversion. Whereas the three catalysts of the SZ series show a fairly similar behavior, in the WZ series, the Pd-containing catalysts were significantly more active than the monometallic Pt one. This second trend is in agreement with the observed in a previous work [23] where activated carbon-supported Pd and Pt catalysts were compared.

Fig 6 shows the selectivity to reaction products of the monometallic Pd catalysts at a space time of 0.8 kg<sub>cat</sub> h (mol DCM)<sup>-1</sup> and different reaction temperatures. As depicted in Fig. 5, both Pd catalysts yielded high DCM conversions at the highest temperature tested (250 °C) although the WZ-supported was significantly more active (93% DCM conversion versus 82% of the SZ-supported). The selectivity curves obtained for the rest of the catalysts are reported as



Fig. 4. Detail of the XRD patterns of Fig. 3.



**Fig. 5.** DCM conversion upon HDC at a space time of 0.8  $kg_{cat}$  h (mol DCM)<sup>-1</sup> and different reaction temperatures with the SZ and WZ catalysts.



Fig. 6. Selectivity of monometallic Pd catalysts at a space time of  $0.8~kg_{cat}~h~(mol~DCM)^{-1}$  and different reaction temperatures.

Supplementary information. Hydrodechlorination of DCM with all the catalysts tested vielded the following non-chlorinated reaction products: methane, ethane, propane, *n*-butane, and 1-butene. In addition, propylene and ethylene were detected but only in the long-term experiments performed for analyzing the stability of the catalysts. All the catalysts were very selective to non-chlorinated byproducts and the selectivity to monochloromethane (MCM) decreased when increasing the temperature with the exception of the monometallic Pt catalysts (SZ Pt and WZ Pt) where that selectivity remained almost constant within the temperature ranged tested (see Supplementary information). At the highest temperature tested (250 °C), the selectivity to non-chlorinated byproducts ranged between 80% and 90%. The main reaction product was always methane with selectivities from around 60% up to more than 85% (for SZ Pt-Pd at 250 °C). As a general conclusion, the selectivity to methane was lower with the WZ-supported catalysts, especially with the WZ Pd catalyst. In previous works [27,51] dealing with the HDC of DCM, higher selectivities to methane were observed with well-dispersed Pd/C and Pt/C catalysts with higher proportions of metal in the zero-valent state. The formation of hydrocarbons higher than CH<sub>4</sub> has been previously related to the electro-deficient metal species, and the presence of large agglomerated metal particles [22,25,27,52]. This is in agreement with our results, where those large particles were observed by XRD in the WZ-supported catalysts (Fig. 4). Previous works on the hydrodechlorination of DCM and carbon tetrachloride with carbon-supported Pd catalysts [22,25,52] showed the existence of dual active sites formed by the connection of adjacent zero-valent and electrondeficient palladium species ( $Pd^{0} + Pd^{n+}$ ). In these cases, hydrogen chemisorbs and homolytically dissociates on Pd<sup>0</sup>, while the chloromethane molecule is chemisorbed on  $Pd^{n+}$ . Therefore, Table 4

Selectivities to the main products at different reaction temperatures at a fixed DCM conversion of 50%.

	<i>T</i> (°C)	S <sub>CH4</sub> (%)	S <sub>MCM</sub> (%)
SZ Pt	214	72.7	24.7
SZ Pt-Pd	220	79.6	19.3
SZ Pd	209	78.1	18.2
WZ Pt	224	71.7	23.5
WZ Pt-Pd	172	67.1	30.3
WZ Pd	173	58.2	38.3

the formation of hydrocarbons of more than one C atom seems to be associated with the reaction of two organochloride radicals adsorbed on neighboring electro-deficient metal sites. Thus, a lower concentration of these sites on the catalyst would reduce the formation of those byproducts, and according to previous works [52], when they are formed, the temperature has a significant effect on the products distribution, the selectivity to those species being favored in detriment of methane by increasing the temperature. In our case, slightly higher selectivities to hydrocarbons higher than methane ( $C_2H_6$ ,  $C_3H_8$ , and  $i-C_4H_{10}$ ) were observed with the WZ-supported catalysts as well as an increase in the selectivity to these compounds with the reaction temperature, which could be consequence of higher amounts of electrodeficient species in these catalysts.

Table 4 compares the selectivity to the main products, namely  $CH_4$  and MCM, at different temperatures at a fixed DCM conversion of 50%. As can be seen in this table, in general trend, the catalysts of the SZ series yield higher selectivities to non-chlorinated byproducts. This support appears to favor the supply of  $H_2$  to the active centers as lower selectivities to MCM are obtained at all reaction temperatures (see data for SZ Pd and WZ Pd in Fig. 6). Nevertheless, the high MCM selectivity values obtained for WZ Pd and WZ Pt–Pd at 50% conversion can be attributed to the lower reaction temperature, which has a marked influence in the selectivity to this product (Fig. 6). The comparison of the selectivities to the different reaction products with the reaction temperature suggests that increasing the temperature gives rise to higher selectivities to non-chlorinated byproducts.

# 3.3. Catalysts stability

In the literature, the deactivation of the catalysts in HDC is attributed to poisoning by HCl and other chlorine compounds, deposition of coke or organochloride species, metal sintering, loss of metal by the formation of volatile compounds and changes in the oxidation state of the metal [4,15–20,53,54]. In general, the catalysts show an initial unsteady state with a significant decrease in the activity before a steady residual activity is reached. The development of highly stable catalysts for hydrodechlorination and the analysis of the causes of deactivation has received increasing attention [27,55,56,20,57–61].

Fig. 7 shows the evolution of DCM conversion upon time on stream (tos) in long-term experiments performed at a space time of 0.8 kg<sub>cat</sub> h (mol DCM)<sup>-1</sup> and 250 °C with the SZ and the WZ catalysts. All the catalysts supported on tungstated zirconia (WZ series) showed a very poor stability regardless of the metal active phase. On the contrary, the SZ-supported catalysts containing Pd exhibited a highly stable behavior, especially in the case of the bimetallic catalyst. It can be seen that the SZ Pd catalyst suffers a slow but monotonical loss of activity upon the 80 h on stream of the experiment, whereas the SZ Pt–Pd showed no deactivation and even a sustained increase in DCM conversion with time on stream was observed. The TPR profiles of these two catalysts (Fig. 1) suggest a fairly uniform distribution of the metallic particles, more remarkable in the case



**Fig. 7.** Evolution of DCM conversion upon time on stream in long-term experiments with the catalysts tested (space time =  $0.8 \text{ kg}_{cat} \text{ h} (\text{mol DCM})^{-1}$ ; T = 250 °C).

of the bimetallic catalyst, whose XRD spectrum (Fig. 2) and CO chemisorptions metal dispersion value (Table 2) suggest also a good dispersion of the metallic particles, which are predominantly located on the outer surface of the support as suggested by XPS results of Table 2. These features must favor the adsorption, desorption, and spillover of reactants and/or reaction products which in turn enhances the deep hydrogenation of chlorocarbons and hinders their irreversible adsorption on the active sites. Fig. 7 shows an apparent initial decline of conversion upon time on stream for SZ Pt–Pd and SZ Pd suggesting some surface restructuring. Several authors ascribe some surface restructuring of metallic particles to the effect of HCl, which they report to provoke the formation, volatilization, and re-deposition of unstable metallic chlorides [15,62]. These chlorides would be reduced under the high concentration of H<sub>2</sub> introduced as reactant

Fig. 8 depicts the selectivity to reaction products upon time on stream from the experiment of Fig. 7 for the highly stable SZ Pt–Pd catalyst. After the initial transition period, no significant changes in the selectivities to the different reaction products were observed. As stated before, methane was the main reaction product with a selectivity around 80% and the selectivities to the chlorinated byproduct, MCM, remained relatively low at around 15%. The rest of the reaction products (total selectivity lower than 5%) were mainly ethane with lower amounts of propane and traces of *n*-butane and 1-butene. A similar behavior was observed for SZ Pd catalyst (see Fig. S5 of Supplementary information), the other one showing a fairly stable behavior (Fig. 7).

For the sake of comparison, Fig. 9 shows the evolution of selectivity to reaction products upon time on stream for one of the catalysts that suffered rapid deactivation (WZ Pt–Pd). For the rest of the catalysts, these results are provided as Supplementary



**Fig. 8.** Selectivity to reaction products of the SZ Pt–Pd catalyst upon time on stream (space time =  $0.8 \text{ kg}_{cat} \text{ h} \text{ (mol DCM)}^{-1}$ ; T = 250 °C).



**Fig. 9.** Selectivity to reaction products of the WZ Pt–Pd catalyst upon time on stream (space time =  $0.8 \text{ kg}_{cat} \text{ h} \text{ (mol DCM)}^{-1}$ ; T = 250 °C).

information (Figs. S6–S8). Methane was always the main reaction product, and in general, no significant variations of selectivity were observed along the experiment. Deactivation seems to inhibit somewhat the deep hydrogenation of the olefinic byproducts as indicated by the slow decrease in the selectivity to alkanes other than CH<sub>4</sub> (ethane, propane, and *n*-butane) and the increase in that to ethylene and propylene, which can be appreciated in Fig. 9. The SZ Pt catalyst was the only one suffering a great deactivation among the SZ-supported catalysts tested. This can be explained by its higher interaction with the support as evidenced by TPR (Fig. 1). In this catalyst, the metallic particles are more equally distributed between the outer surface and the internal porosity (Table 2) and a higher proportion of electrodeficient Pt was measured by XPS (Table 3).

# 3.4. Characterization of the used catalysts

The XRD patterns (not represented) of the SZ and WZ catalysts after used in the long-term experiments showed no significant changes with respect to those of the fresh reduced ones. This suggests that no significant modification of the size of the metallic particles takes place during the HDC process. Table 5 shows the bulk elemental analyses of the fresh and used catalysts. It is noteworthy the increase in carbon content of all the catalysts after use which is significantly more accused in those showing faster deactivation (see Fig. 7). These results support the strong adsorption of organic species that would provoke blockage of the active sites

#### Table 5

Elemental C and S content of the fresh (reduced) and used catalysts.

	%C	%S
Fresh catalysts		
SZ Pd		1.42
SZ Pt		1.40
SZ Pt-Pd		1.30
Used catalysts		
SZ Pd	0.18	0.90
SZ Pt	1.49	0.03
SZ Pt-Pd	0.76	0.43
WZ Pd	1.26	
WZ Pt	2.25	
WZ Pt-Pd	1.00	



**Fig. 10.**  $N_2$  adsorption–desorption isotherms (77 K) of SZ Pt–Pd and WZ Pt catalysts fresh and after used in the hydrodechlorination of DCM.

as a cause of deactivation. The surface concentration (as determined by XPS) of Cl of the low-stability WZ catalysts used was between three and five times higher than in the fresh ones, thus supporting the adsorption of chlorine-containing organic species on the used catalysts. Table 4 also shows a significant reduction of the sulfur content of the SZ catalysts after use. It is known that the catalysts based on sulfated zirconia can lose sulfur when submitted at a relatively high temperature in the presence of hydrogen [63,64]. This decrease in sulfur is due to the  $SO_4^{=}$  reduction to  $SO_2$ , which in the presence of platinum is further reduced to H<sub>2</sub>S. According to van Gestel et al. [65],  $SO_4^=$  can be reduced at temperatures as low as 150 °C in the presence of platinum. Therefore, the presence of Pt would favor the loss of sulfur of the SZ-supported catalysts in agreement with the results reported in Table 4. The  $H_2S$  formed upon  $SO_4^-$  reduction would provoke poisoning of Pt thus explaining the poor stability of the SZ Pt catalyst in contrast to SZ Pd and SZ Pt-Pd. In fact, although the bulk S content of the SZ Pt catalyst used is very low (0.03%w in Table 4), the surface S concentration as determined by XPS was 0.5%w.

Fig. 10 depicts the 77 K  $N_2$  adsorption-desorption isotherms of SZ Pt–Pd and WZ Pt catalysts fresh and after used in the hydrodechlorination of DCM. We have represented the results of a catalyst with high stability (SZ Pt–Pd) and one of the catalysts with a high deactivation rate (WZ Pt). In the case of the highly stable catalyst, the decrease in the amount of  $N_2$  adsorbed is almost negligible, indicating that no blockage of the porous structure of this catalyst takes place during the hydrodechlorination reaction. Only a very slight reduction in the amount of  $N_2$  adsorbed at low relative pressures is observed, which suggests a low significant reduction in the micropore volume. On the opposite, WZ Pt catalyst shows a significant reduction in the volume of N<sub>2</sub> adsorbed at high relative pressure ( $P/P_0 > 0.8$ ) indicative of a significant decrease in available mesopores during the dehydrodechlorination reaction. This behavior is in agreement with the lower amount of carbon and/or chlorinated organic compounds deposited on the surface of the more stable catalysts (SZ Pd and SZ Pt–Pd), as shown by ultimate analyses and XPS, in contrast to the significant increase in the amount of carbon and chlorine observed for the catalysts that suffer deactivation, possibly because of the deposition of chlorinated organic species onto the mesopores blocking the accesses to the reaction sites.

# 4. Conclusions

The Pd and Pt mono- and bimetallic catalysts prepared using zirconia promoted with sulfate (SZ) and tungsten oxide (WZ) as supports were fairly active in the hydrodechlorination reaction of DCM; though, in general, the WZ catalysts yielded significantly higher DCM conversion values than the SZ ones. All the catalysts were very selective to non-chlorinated reaction products, the higher selectivities being obtained with the sulfated zirconia-supported Pd-Pt and Pd catalysts. The selectivity to monochloromethane decreased when increasing the reaction temperature except with the monometallic platinum catalysts where that selectivity remained almost constant within the temperature range tested (150-250 °C). Methane was the main reaction product in all the cases. Ethane, propane, *n*-butane, and 1-butene were also identified as byproducts. In addition, ethylene and propylene were detected in long-term experiments. The catalysts supported on tungstated zirconia showed a very poor stability regardless of the metal active phase. On the opposite, the palladium-containing catalysts supported on sulfated zirconia showed a high stability, in particular the bimetallic catalyst, demonstrated in long-term experiments (80 h on stream). The high stability of SZ Pt-Pd catalyst can be ascribed to the smaller size of metallic particles and their uniform distribution on the outer surface of the support, which inhibits the poisoning of active centers by chlorinated organic species. Deactivation of the other catalysts can be attributed to the deposition of chlorinated organic species blocking the active sites and, in the case of SZ platinum catalyst, also to poisoning by the H<sub>2</sub>S resulting from  $SO_4^-$  reduction in the presence of hydrogen.

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# Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2012.07.023.

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